

## EXAFS studies on colloidal Ni particles stabilized with *t*-BuONa

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### Introduction

Ni catalysts are very useful for many catalytic reactions. But the size of Ni particles on catalyst is typically 20 - 100 nm. It is difficult to prepare small Ni particle on the support because of magnetic attractions of Ni metal. The study on the nano-sized Ni catalysts is very few.

Colloidal metal particles have been expected as a superior catalyst precursor for supported solid catalyst because of their small particle size and the narrow size distribution. But the stabilizer, which is needed to synthesize metal colloid, remained on the metal surfaces and lead to lower the effective metal surface area as well as the catalytic activity. Thus, the diminishment of the stabilizer would be expected.

In this study, we prepared Ni metal colloid by using *t*-BuONa as a stabilizer. Effect of the stabilizer amount on Ni particle size and chemical state was studied by EXAFS analysis.

### Experimental

The overall preparation process of Ni colloid was carried out under  $N_2$  atmosphere. Ni colloid was synthesized by reduction of  $Ni(OAc)_2$  using  $NaH-t$ -BuONa in refluxing THF at 336 K [1]. The ratio ( $R_s$ ) of *t*-BuONa to Ni was changed between 1.0-10.0. Prepared colloids were denoted with the  $R_s$  as Ni colloid-1.0

Ni K-edge EXAFS spectra were measured at BL-9C and 12C of the Photon Factory with Si(111) double crystal monochromator. The Ni colloidal solution was measured in fluorescence mode using Lytle detector. Curve-fitting analyses of  $k^3$ -weighted EXAFS oscillations in the  $k$ -space were performed by the EXAFS analysis program REX2000 (Rigaku Co.). Model parameters for curve-fitting analysis (back scattering amplitude and phase shift) were extracted from an EXAFS oscillation collected for bulk Ni ( $N=12$ ,  $r=0.249$  nm).

### Results and discussion

$Ni(OAc)_2$  was reduced to Ni metal by  $NaH-t$ -BuONa. The excess amount of *t*-BuONa also acted as a stabilizer.

FT of Ni K-edge EXAFS spectra for Ni colloids was shown in Fig. The FT profile of Ni colloid-1.0 and 2.0 was similar to that of bulk NiO. On the other hand, Ni species in Ni colloid-5.0 and 10 was in metal state. It can be said that the  $R_s$  must be larger than 2 to produce Ni metal colloid.

Although colloidal Ni metal particles were produced and stabilized with  $R_s \geq 5$ , Ni particles were easily oxidized to NiO by exposing to the air at r. t., as shown in Fig.

Coordination numbers (CNs) of Ni-Ni were listed in Table. CN in Ni colloid-5.0 and Ni colloid-10 were 2.9 and 4.1, respectively. The 2nd and 3rd nearest Ni-Ni coordination was not observed. The size of Ni particles in these colloidal Ni solutions could be estimated as less than 2 nm.

As impregnating  $SiO_2$  with these colloidal Ni solutions for the preparation of Ni/ $SiO_2$  catalyst, the supported Ni is in oxidized state. The catalyst has to be treated with hydrogen at 573 K to applying the catalytic reaction. After the hydrogen treatment at 573 K, Ni particles on the  $SiO_2$  remained less than 2 nm. The small Ni particles could be prepared on  $SiO_2$  by using Ni colloidal solutions as precursor.

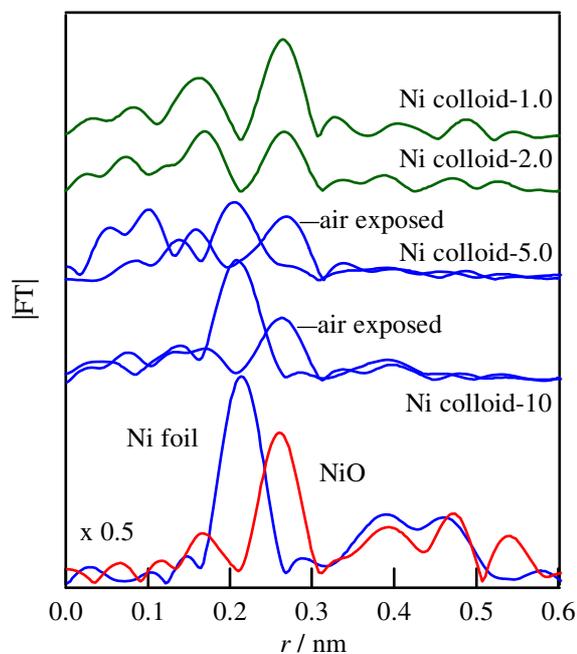


Figure. FT of  $k^3$ -weighted Ni K-edge EXAFS for colloidal Ni particles and reference compounds.

Table: Curve fitting result for Ni-Ni coordination

sample	N	$r$ / nm	$dE$ / eV	DW / nm
Ni colloid-5.0	2.9	0.246	-8.586	0.0072
Ni colloid-10	4.1	0.247	-5.900	0.0066
bulk Ni	12	0.249	0.0	0.006

### Reference

- [1] Pierre Gallezot, Christiane Leclercq, Yves Fort and Paul Caubere, *J. Mol. Catal.*, **93**, 79-83 (1994)

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